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BULGER WAFER AND ADJUNCTS

FOR FALLOUT SHELTER RATIONS

A report of research conducted July 1965 - June 1966

by

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SUMMARY

Product stability is probably the dominant problem in maintaining large stocks of fallout shelter rations. To assure that the food in storage is edible, it must be monitored. For this surveillance testing, a reliable objective measurement of quality is needed, in order to avoid the expense and variability of taste evaluations.

Knowledge of the mechanism of oxidative deterioration should facilitate the development of such a test for the bulgur wafer. Further identification of oxidative products and their mechanisms has been achieved principally by use of gas liquid chromatography and mass spectrometry. Eleven acids have been identified from autoxidized methyl linoleate. Evidence has accumulated that early-appearing carbonyls are involved in secondary reactions that produce the more stable compounds appearing later in the oxidation process.

Major emphasis during FY 1965 has been to correlate the time of appearance of stable volatile components from oxidizing bulgur with oxygen uptake and off-flavor development. Pentane, carbon dioxide, carbon monoxide, and hexanal development up to 18 weeks has generally followed a typical unsaturated-fat oxidation curve. Oxygen uptake shows a similar curve.

Hexanal levels in puffed bulgur stored under oxygen at elevated temperatures did not parallel off-flavor development over long periods of storage. After 15 months, hexanal values had dropped lower than those found when rancidity was first detected.

Wheat germ oil was evaluated as a model system for studying oxidation of bulgur but was rejected because of its very slow rate of oxidation.

Taste panel evaluations through 40 months of storage continue to show a protective influence of nitrogen packing on flavor of wafers stored at 70° and 100°F. Other treatment variables are relatively unimportant in nitrogen-packed samples.

When changes in flavor score with storage time are considered, again the favorable influence of nitrogen packing upon wafer quality is apparent. The flavor scores for the reference formulation and pack (pressure-cooked bulgur, malt sirup binder and nitrogen pack) did not change significantly with time, regardless of storage temperature. Similarly, all air-packed samples stored at 40°F did not change significantly with time, regardless of formulation.

Air-packed samples stored at 70°F and 100°F show the only major changes in flavor score with time, but in no case have the scores dropped to 4, dislike slightly.

Of the objective tests being investigated for possible use in surveillance testing of the wafers, carbon monoxide content of the headspace gas appears to be the most promising. Correlation between this analysis and taste panel scores for 22, 28, and 34 months' storage for all formulation at all temperatures are significant at the 1% level.

Results of panel evaluations after 30 months' storage of twelve selected adjuncts indicate a protective action by nitrogen packing on all adjuncts except apple topping, wild cherry icing, strawberry spread and beef soup. Among the seven adjuncts for which in-package desiccant (IPD) is a treatment variable, samples with IPD scored higher for all except Oriental sauce, chili sauce, and beef soup. The effects of high temperature are especially demonstrated by the lower flavor scores given chicken soup, curry sauce, and Oriental sauce stored at 100°F

Expert panel evaluations of the adjuncts before, during, and after preparation reveal that certain treatments of some of the adjuncts are not performing well, and can corrosion has been noted in some instances. In general, flavor scores are staying up reasonably well, at least for nitrogen-packed and/or IPD samples so that it would appear that ease of preparation (or actually lack of it) may be the first limiting factor for some adjuncts.

Carbon monoxide content of the headspace gas above the adjunct has been found to show a significant correlation with flavor score for seven of the adjuncts, but only the data from 24 and 30 month sampling periods are available.

BULGUR WAFER AND ADJUNCTS FOR FALLOUT SHELTER RATIONS

SECTION 1

DEVELOPMENT OF NEW STABILITY EVALUATION METHODS

Efforts have been continued to develop reliable objective measurements that correlate with taste panel appraisal, for use in surveillance testing of stored bulgur wafers. The premise that unsaturated fatty acids of wheat lipids in bulgur shelter wafers are the components most likely to limit wafer shelf-life appears to be supported by our experimental results.

In the last year, wheat germ oil was evaluated as a model system for studying the oxidation of bulgur but was rejected because of its slow rate of oxidation. Therefore, methyl linoleate continues to serve as a model system because of the many parallels found between its chemical behavior and that of various bulgur products. Also, linoleic acid constitutes more than 50% of the fatty acids in the lipids of bulgur and puffed bulgur.

In addition to the model compound study, work has been done to correlate the time of appearance of various volatile compounds from oxidizing ground puffed bulgur with oxygen uptake and off-flavor development.

A Model System - Methyl Linoleate

Work has continued on identification of compounds from autoxidized methyl linoleate. Several analytical techniques have been employed, principally capillary gas liquid chromatography (GLC) coupled with rapid-scan mass spectrometry (MS), but also preparative GLC, infrared spectroscopy (IR), and nuclear magnetic resonance (NMR).

Acid fraction

Several acids were identified in the residue of fairly highly oxidized methyl linoleate (peroxide value, 1000 millimols/kg.) from which the volatile components had been removed by distillation at 10-20 microns. The acidic compounds were extracted by dissolving the residue in ether and washing it with several volumes of dilute sodium bicarbonate. The extracted acids were converted into their methyl esters with diazomethane and analyzed by means of capillary GLC-rapid scan MS. In addition, all of the major components of this fraction were separated by means of preparative GLC and analyzed by IR, NMR, and MS.

The major acids found were: formic, hexanoic, <u>trans</u>-2,3-epoxyoctanoic, suberic, and azelaic; the last one represents about 80% of the acids. The structure of methyl 2,3-epoxyoctanoate was established by synthesis of an authentic sample of this epoxyester from the reaction of bromomethylacetate and hexanal. This synthesized ester was separated into its two isomeric forms by means of preparative GLC. The GLC retention time and the IR spectrum for one form were identical with those for the compound from autoxidized methyl linoleate. The configuration of the epoxide ring in the isolated ester was shown, by NMR, to be <u>trans</u>. Minor components of the acid fraction included pentanoic, heptanoic, 2-heptenoic, 2-octenoic, octanoic, and nonanoic acids.

Some components of the acid fraction are quite pungent and could contribute significantly to off-flavor development in stored bulgur products. Formic acid, for example, has a very sharp odor. Pentanoic and hexanoic have a strong goaty odor, and methyl <u>trans</u>-2,3-epoxyoctanoate possesses a rancid type of aroma. Some of the minor acids were synthesized in order to obtain a sufficient amount for flavor evaluation; several of them were found to possess strong characteristic odors. However, simple precise methods for analysis are lacking so none of the acidic components seem as potentially useful for development of an objective surveillance test as other volatile compounds being evaluated.

Low-level oxidation

Comparisons were made of constituents produced from autoxidizing methyl linoleate at low and at high peroxide values. The purpose was to elucidate the nature of the secondary reactions of the aldehydes and other reactive compounds and the contribution these secondary reactions might make to organoleptic properties of the sample at various stages of autoxidation.

Analysis of the volatiles from the sample having a high peroxide value (1000 millimols/kg.) showed only trace amounts of 2-heptenal and 2-octenal, although other workers have reported these two compounds to be present in fair quantities. When the autoxidation was allowed to proceed only to a peroxide value of 150-200 millimols/kg., the volatiles did show high concentrations of these two aldehydes. Thus it appears that 2-heptenal and 2-octenal were oxidized to the corresponding acids, which were identified in the residue of highly oxidized methyl linoleate.

Two compounds, acetone and 2-methyltetrahydrofuran, not previously identified in highly oxidized methyl linoleate were also found in the volatiles from the low-level oxidation. These compounds are apparently consumed in secondary reactions during prolonged oxidation.

Furthermore, only one dioxolane, the 2,4-dipentyl, was found at low-level oxidation, whereas four different dioxolanes were observed in more highly oxidized methyl linoleate (Bulgur Wafers and Adjuncts for Fallout Shelter Rations, FY 1965, p. 5). When the volatile fraction was stored at 0°C for two weeks and then analyzed by capillary GLC, peaks with retention times corresponding to the other substituted dioxolanes appeared. Therefore, it appears that the dioxolanes can be formed by secondary reactions of certain aldehydes and an unknown compound in the volatile fraction.

All these findings suggest several secondary reactions which can consume aldehydes formed in early stages of oxidation and could explain the discrepancy between formation of aldehydes (especially hexanal) and off-flavor development in bulgur products.

A Model System - Wheat Germ Oil

In order to determine if wheat germ oil could be used as a model system, 20 g of it was spread as a film on clean glass wool and exposed to purified oxygen. The rate of oxygen consumption over a 4-week period was negligible, and the peroxide value of the oil was very low. In comparison, methyl linoleate would have attained a peroxide value of about 1000 millimols/kg.

GLC analysis of an isooctane extract from the vacuum distillate of autoxidized wheat germ oil showed the presence of several rolling peaks, presumably short-chain fatty acids. Noticeably absent from the volatiles of oxidized wheat germ oil were peaks with retention times corresponding to aldehydes, esters, and hydrocarbons commonly found in oxidized lipids rich in linoleic acid.

The rate of oxidation of linoleic acid in triglycerides has been estimated to be half that of linoleic acid in methyl linoleate, based on studies with safflower oil (Private communication, Glenn Fuller, WRRL). We found the rate in wheat germ oil to be about one-fiftieth that in methyl linoleate. The extreme resistance of the oil to oxidation is probably due to the high level of tocopherols (0.1% of the oil), which are destroyed in conversion of wheat to bulgur. For this reason, wheat germ oil was considered unsatisfactory as a model system for studying oxidation of bulgur products unless some is found in which the antioxidant has been removed or inactivated.

Components of Bulgur Vapors

In the past year, work has continued to identify the volatiles from autoxidizing ground puffed bulgur. Some effort was made to obtain a fraction of these volatiles sufficiently concentrated to

use with capillary GLC coupled with rapid-scan MS. A volatile fraction from ground puffed bulgur, judged rancid, was obtained by the use of vacuum steam distillation. GLC analysis of the pentane extract of this volatile fraction revealed 15 major components. However, the absence of several low-boiling compounds found in the volatiles from oxidized methyl linoleate indicates that vacuum steam distillation, as used in this work, may not be a suitable method for isolating the volatiles from autoxidizing ground puffed bulgur. Further work will be required to find an isolation technique that produces a representative volatile fraction.

Acceleration of Rancidity

Both oxygen and high temperature continue to be used for accelerating off-flavor development in ground puffed red wheat bulgur.

Storage of puffed bulgur

The storage study previously reported (Bulgur Wafer and Adjuncts For Fallout Shelter Rations, 1965, p. 10), which attempted to correlate hexanal concentration with off-flavor development in hot-air-puffed ground bulgur sealed under oxygen and stored at 34°, 70°, 90°, and 100°, was concluded after 15 months. Controls consisted of samples stored under nitrogen at the same temperatures. Headspace gas (1 to 3 ml) was removed from each can and analyzed for hexanal by means of GLC. The concentration of hexanal in the headspace gas was estimated by comparing the area of the hexanal peaks in the GLC chromatograms with the area of peaks produced by samples of air containing known quantities of benzene as a stable reference compound. A small panel judged the development of rancidity in the same sample on which headspace gas analysis was run. Changes in hexanal content of headspace gas during the test period are shown in Table 1.1.

At six months' storage, only the 90° and 100° samples were judged rancid. After 15 months, all but the 34° sample were judged rancid, but hexanal values were lower than found in early stages of storage when no rancidity was detected. No hexanal was detected in nitrogen-packed controls except for a trace in the 15-month 100° sample. This series of experiments demonstrates conclusively that the degradative reactions are primarily oxygen-induced and that while hexanal development might be a useful tag for continuous monitoring it is essentially useless for spot surveillance.

If, as suggested earlier in this report on work with model systems, the aldehydes (hexanal) disappear by being consumed in secondary reactions, one or more of the products of these reactions (substituted dioxolane, acetals, acids, etc.) might correlate more closely with rancidity development in bulgur than do the aldehydes.

TABLE 1.1.--Hexanal production of bulgur stored in oxygen

	Months of Storage							
	1	2	3	4	4-1/2	6	7	15
100°F	0	0.04	0.15	0.36	0.61	1.4	2.0	0.2
90°F	0	0.04	0.09	0.27	0.39	1.1	1.6	0.4
70°F	0	0.03	0.08	0.22	0.32	0.6	0.8	0.4
34°F	0	0	0	0	0	0	0	0

All hexanal concentrations = n x 10^{-2} μmoles hexanal/ml of headspace gas.

Oxygen uptake

During autoxidation of methyl linoleate, carbon dioxide, carbon monoxide, hydrogen, pentane, and hexanal appear in detectable quantities at the end of the induction period. If bulgur and related products were found to behave in a similar manner, then the appearance or increase of carbon dioxide, carbon monoxide or pentane might be a useful indicator of incipient rancidification in stored bulgur shelter wafers.

In order to obtain experimental data about oxygen uptake of ground puffed bulgur and the time of appearance of the above mentioned components, 200 g of this material was placed in a flask fitted with a silicone rubber septum connected to a gas burette filled with purified oxygen, and the apparatus maintained at 100°F. Oxygen uptake was measured, and GLC analyses of headspace gas were made three times a week. Even though hexanal has been shown to be a poor indicator for oxidative off-flavor, it was measured in order to correlate its change with the development of pentane.

The oxygen-uptake curve for ground puffed bulgur after 14 weeks was typical of fat oxidation curves (Fig. 1.1). Oxygen uptake was very slow (0.3 to 0.4 ml/day) for the first 2 weeks (induction period), followed by a sharp increase in rate to as high as 9.8 ml/day through the next 8 weeks. The uptake rate declined to 2.0 ml/day after the 10th week.

Headspace gases were analyzed for carbon dioxide, carbon monoxide, normal hydrocarbons (C_1 to C_5), and hexanal. Headspace samples showed measurable amounts of hexanal, pentane, carbon monoxide, and carbon dioxide in 24 hr. The early appearance of these compounds may have been the result of oxidation of the wheat lipids during hot-air puffing and subsequent grinding of the bulgur. Carbon dioxide and carbon monoxide (Fig. 1.2) and pentane (Fig. 1.3) remained at about the same level for 8 weeks, then began to increase rapidly between the 8th to 10th week. Hexanal, however, began to increase in concentration after 6 weeks. The prior identification of all these components from autoxidizing methyl linoleate, coupled with the evidence presented here, further supports our working hypotheses that the shelf life of bulgur products is largely determined by the unsaturated fatty acids present. The rate of formation of these four compounds generally follows curves obtained by other measurements of oxidative degradation of unsaturated fatty acids.

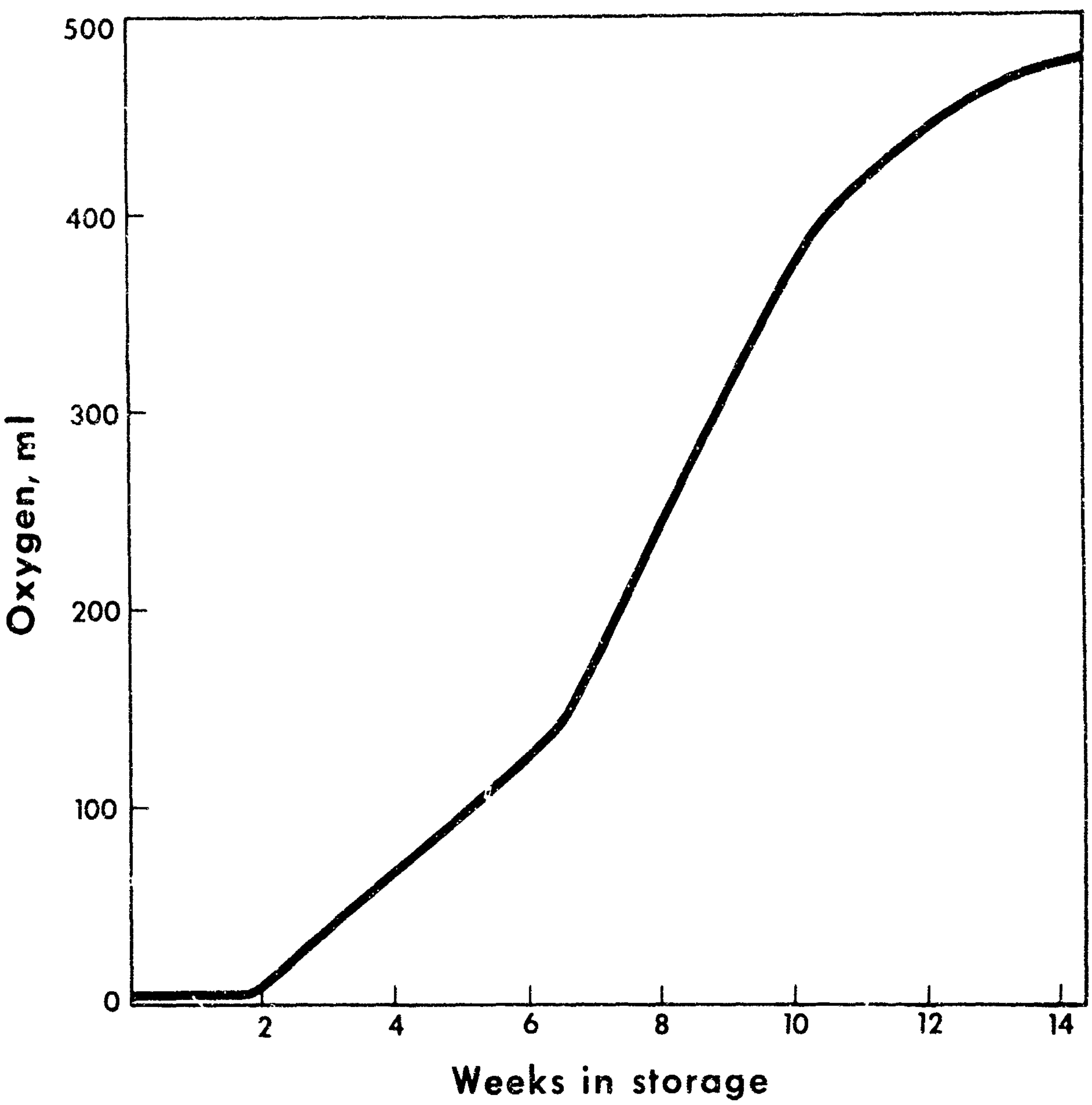

Figure 1.1 Oxygen uptake by puffed ground bulgur in storage at 100°F

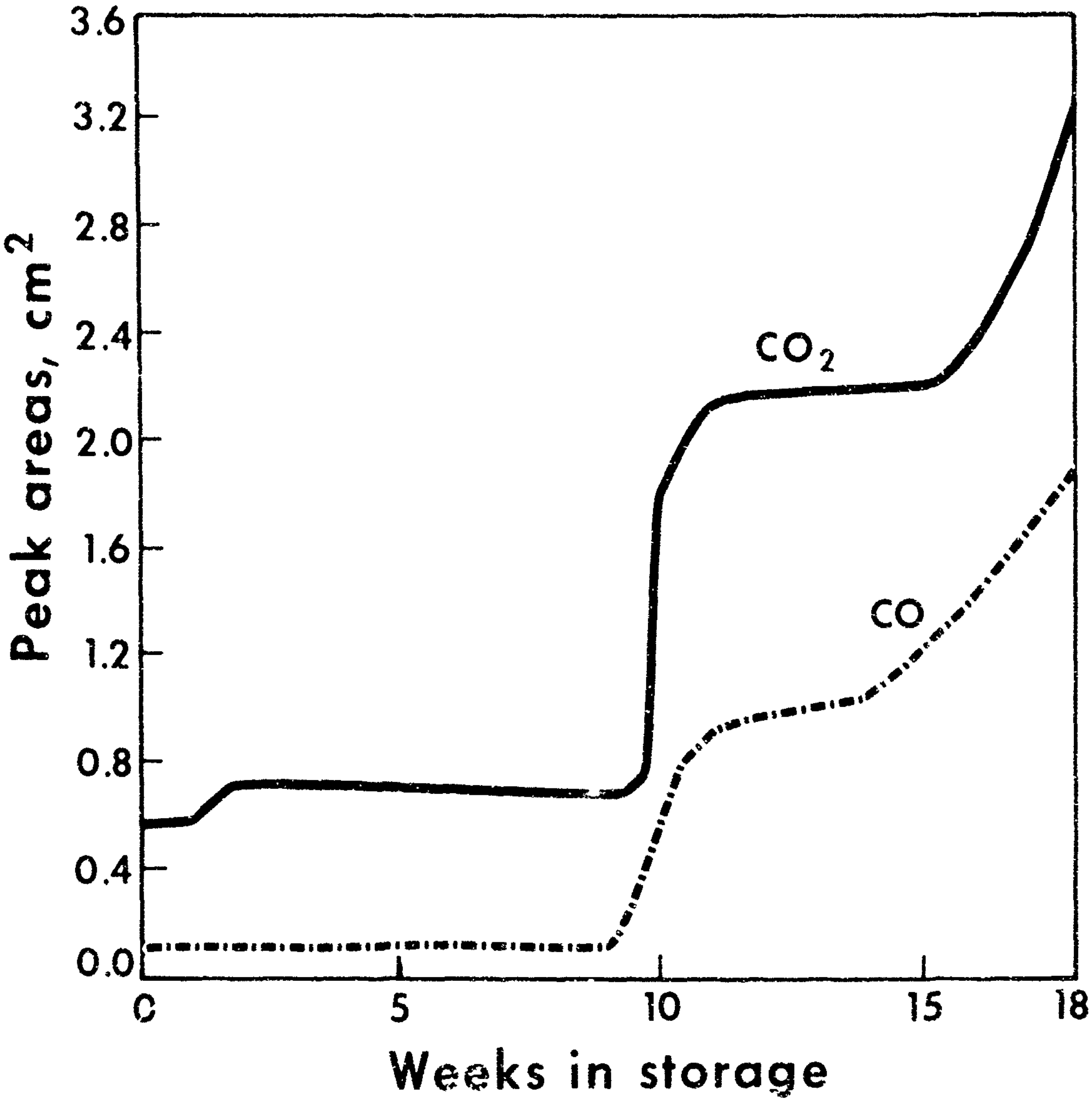

Figure 1.2 Carbon dioxide and carbon monoxide concentration in head space gas above oxidizing puffed ground bulgur stored at 100° F.

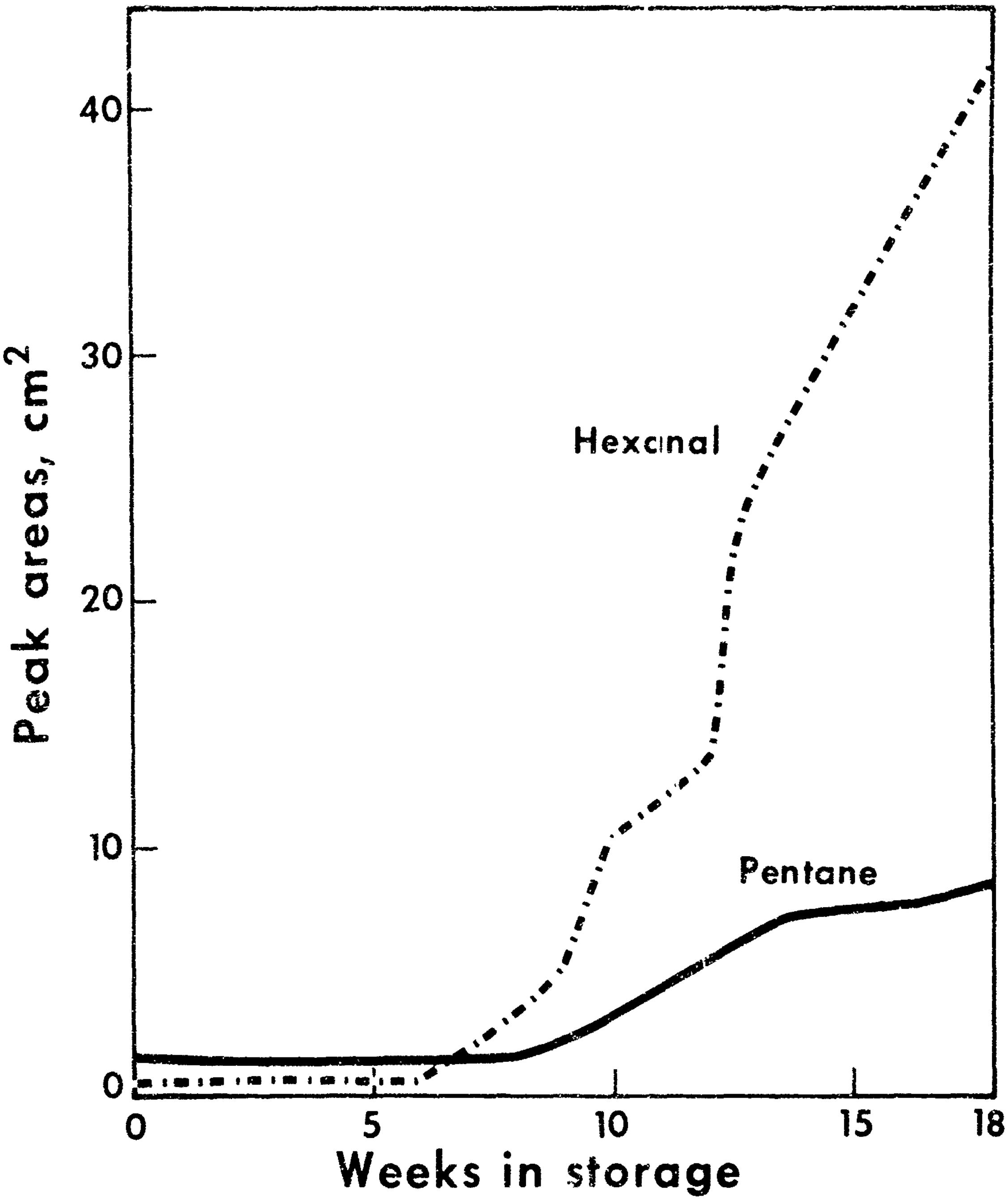

Figure 1.3 Pentane and hexanal concentration in head space gas above oxidizing puffed ground bulgur stored at 100°F.

Several relatively stable and regularly developing compounds have now been identified as occurring during oxidation of both bulgur and the model system methyl linoleate. They are: carbon monoxide, carbon dioxide, and pentane in headspace gas; substituted dioxolanes, acetals, and other secondary reaction products in the volatile fraction of the oils; and pentanoic, hexanoic, azelaic, and other acids in the nonvolatile residue. In order to evaluate them as possible indicators of rancidity development, puffed bulgur will be subjected to accelerated storage tests, and the three fractions indicated (headspace gas, volatile fractions of the lipid, and nonvolatile lipid residue) will be checked periodically by taste panels and by GLC analyses.

SECTION 2

STORAGE STABILITY

Shelter rations must retain acceptable quality during extended periods of storage (in other words, have a long "shelf life"); this is a most important consideration in establishing the true cost of any shelter stocking program. The only true test for shelf life is long-term storage of the rations at the temperatures expected during storage in shelters and warehouses, and evaluation of quality changes by taste panel methods. Objective tests become valid replacements for evaluations by taste panels only after the tests have been shown to be well correlated with taste panel results.

A contract to conduct a 5-year study of the storage stability of bulgur fallout shelter wafers was made with the Department of Food Science and Technology at Oregon State University in June, 1962. A contract with the same group, made in June 1963, provides for a similar study of 12 varied sauces, spreads, etc., selected to serve as adjuncts to the wafers in a shelter ration.

Bulgur Wafers

The contract on wafer stability provides for evaluation of 8 different types of wafers prepared from each of two lots of wheat (one red wheat, one white wheat) and representing all combinations of the following formulations and packaging factors:

1. Pressure cooked vs. atmospheric cooked bulgur,
2. Malt sirup vs. cc sirup as a binder,
3. Air pack vs. nitrogen pack.

To provide the necessary samples, red and white wheats were provided by the Fisher Flouring Mills Co., Seattle, Washington. They processed part of each lot into bulgur by a pressure-cooking process. The remainder was processed into bulgur by atmospheric cooking at the Armeno Cereal Co., Westboro, Massachusetts. All bulgur was puffed and made into wafers by the Van Brode Milling Co., Inc., Clinton, Massachusetts.

The wafers are stored at three temperatures: 40°, 70°, and 100°F. They are sampled and evaluated at 6-month intervals.

Taste-panel evaluation

One formulation each of red and white wheat, those with pressure-cooked bulgur, malt sirup binder, and nitrogen pack were arbitrarily chosen to serve as reference and control samples. The flavor of

control samples, which are held at -18°F, is scored at each sampling period by means of a 9-point hedonic scale ranging from 1 for the lowest to 9 for the highest rating. Results of these judgments through 40 months of storage are given in Table 2.1. At any given sampling time, no significant difference has been found between red and white wheat wafers and no trend has appeared with time. The variation in flavor scores as the test progresses appears to be only variation in taste-panel performance.

At each sampling period the reference formulations (defined above) stored at 40°, 70°, and 100°F are compared with their appropriate red or white controls (stored at -18°F) by means of a reference-preference test on a 9-point hedonic scale. Results of these judgments through 40 months are given in Table 2.2.

Each of the other formulations is then compared, by means of the same kind of a reference-preference test, with its appropriate reference sample stored at the same temperature. Table 2.3 shows mean scores of the samples stored for 40 months and the original mean scores before storage.

Regression lines were calculated for reference-preference scores for reference samples (pressure-cooked, malt sirup, nitrogen pack) (Table 2.2) as a function of time. For all three temperature series, the slopes were essentially zero. This indicates that the flavor score for this formulation and pack did not change with time -- that the hedonic score for flavor is essentially indistinguishable from that for the -18°F controls -- a score of 6.16 (from Table 2.1).

Since the controls stored at -18° do not differ from each other and are not changing, and neither are the reference formulations stored at 40, 70, and 100 , we make the assumption that data for the various formulations stored at 40, 70 and 100 are directly comparable.

The protective effect of nitrogen packing on flavor of wafers stored at 70 and 100°F continues to be pronounced. The estimate of the economic value of inert gas pack previously reported (see report, "Bulgur Wafers and Adjuncts for Fallout Shelter Rations," 1964, p. 2) is still valid; in fact, as storage time increases the argument in favor of gas packing becomes more compelling. While other treatment variables (i.e., binder and type of cooking) influence flavor scores somewhat, they are relatively unimportant in nitrogen-packed samples. The favorable influence of nitrogen-pack on preserving wafers can be shown very clearly when changes with storage time are considered. Some comparisons between oxygen-packed and nitrogen-packed samples are shown in Figure 2.1. Data used to construct this figure are reference-preference scores adjusted to the level of the average hedonic score (6.16).

TABLE 2.1.--Flavor scores[a] on 9-point hedonic scale[b] of bulgur wheat wafers--control samples made from pressure-cooked bulgur with malt sirup binder, packed with nitrogen and stored at -18°F

	Storage time, months							
	0	4	10	16	22	28	34	40
Red wheat	6.40	6.03	5.68	6.53	6.26	6.22	5.95	6.22
White wheat	5.72	6.41	5.82	6.42	6.20	6.39	6.02	6.29
					Overall average		6.16	

[a] 160 judgments.

[b] 9, like extremely; 8, like very much; 7, like moderately; 6, like slightly; 5, neither like nor dislike; 4, dislike slightly; 3, dislike moderately; 2, dislike very much; 1, dislike extremely.

TABLE 2.2.--Reference-preference scores[a] for flavor of reference samples stored at 40°, 70° and 100°F

Averages of data from both red and white wheat wafers

	Storage time, months						
	4	10	16	22	28	34	40
At 40°	5.38	5.32	5.44	5.34	5.24	5.33	5.21
At 70°	5.29	5.24	5.26	5.28	5.21	5.30	5.20
At 100°	5.23	5.01	5.29	5.23	5.11	5.10	5.05

[a] 80 judgments. 9, extremely better than control stored at -18°F; 8, very much better; 7, moderately better; 6, slightly better; 5, neither better nor worse than control; 4, slightly poorer than control; 3, moderately poorer; 2, very much poorer; 1, extremely poorer.

TABLE 2.3.--Reference-preference scores[a] for flavor of bulgur wafers, initially and after 40 months of storage

Averages[b] of data from both red and white wheat

Packaging	Binder	Initial scores		Stored 40 months at:					
				40°F		70°F		100°F	
		A[c]	P[c]	A	P	A	P	A	P
In nitrogen	Malt	5.57	5.27	5.53	4.91	5.51	5.28	5.34	5.39
	Corn	5.38	5.41	5.25	5.11	5.12	5.16	5.17	5.04
In air	Malt	5.44	5.35	5.52	5.11	3.99	3.81	4.75	4.74
	Corn	5.10	4.92	5.17	5.05	3.97	3.60	4.48	3.98

[a] 9, extremely better than reference; 8, very much better than reference; 7, moderately better than reference; 6, slightly better than reference; 5, neither better nor poorer than reference; 4, slightly poorer than reference; 3, moderately poorer than reference; 2, very much poorer than reference; 1, extremely poorer than reference.

[b] 80 judgments per sample.

[c] A = atmospheric-cooked bulgur; P = pressure-cooked bulgur.

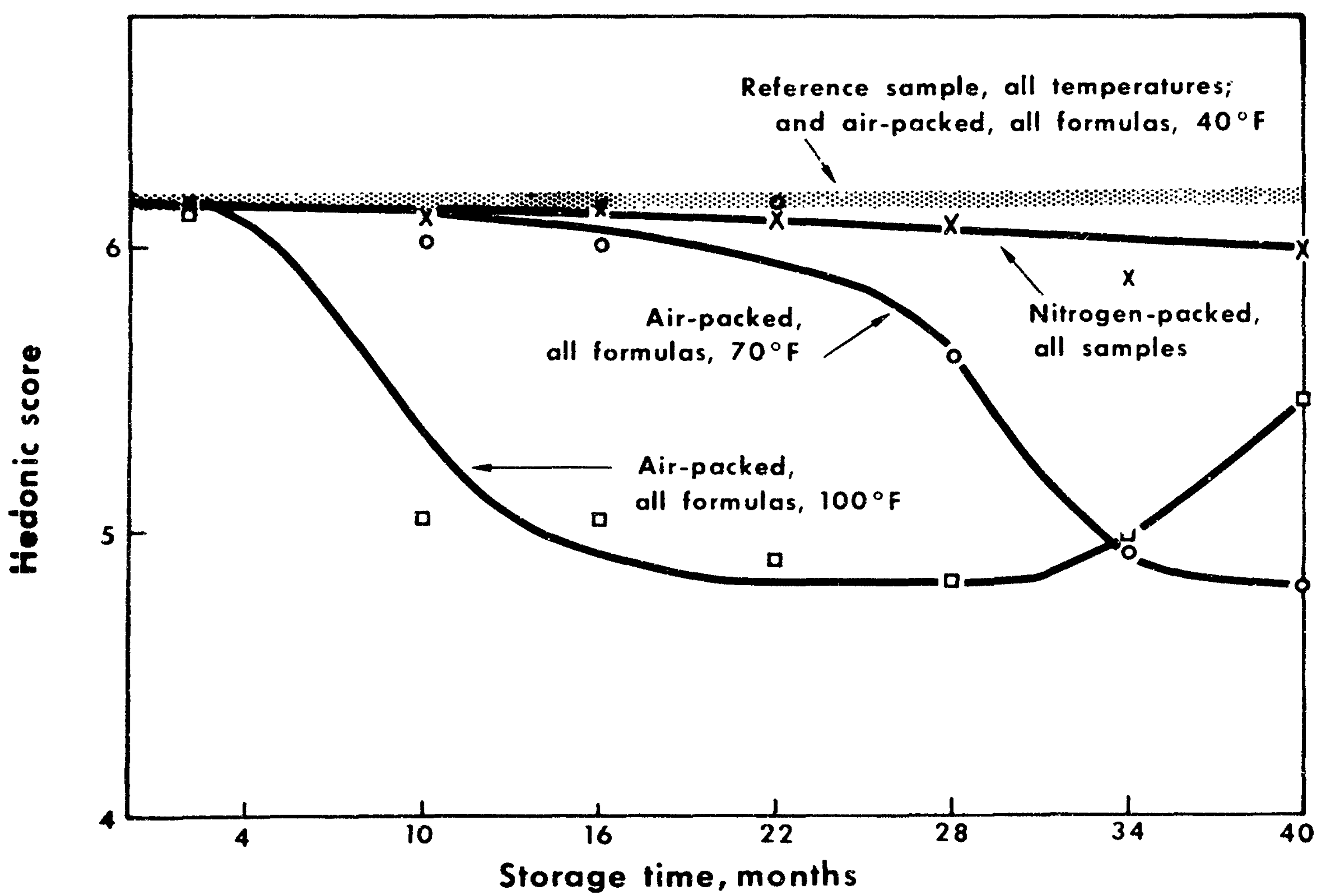

Figure 2.1 Flavor score of wafers as influenced by storage time and temperature, formulation, and packaging atmosphere.

A regression coefficient for the change with time in reference-preference scores of all air-packed samples stored at 40°F was found not to differ significantly from zero. Average scores of nitrogen-packed samples, including all formulations at all temperatures, show a slight but significant negative regression on time The curves for air-packed samples stored at 70° and 100°F (Fig. 2.1) show the only major changes in flavor scores with time, and the trends are not linear. At 100°F there was an almost immediate drop in score followed by a leveling off to about 34 months. Whether the rise at 40 months is real or not will be answered by subsequent samplings. At 70°, flavor score decreased slowly at first, but after 22 months the rate increased until at 34 months the scores were about equal to those at 100°F

The data shown in Figure 2.1 present very convincing evidence for nitrogen packing. The reference samples (which were nitrogen-packed) were as stable at the higher temperatures as were the air-packed samples stored at 40°F; any formulation under nitrogen deteriorated very slowly, even at 100°F.

Furthermore, adjustment of the reference-preference scores to a level equivalent to the average hedonic score (as has been done in Fig. 2.1) shows that, although the scores for air-packed samples at 70° and 100°F have dropped substantially, they have not yet reached a score as low as "dislike slightly" (hedonic = 4).

Chemical-physical determinations

At each sampling period, each lot of wafers is analyzed to determine percentage fat, peroxide number, thiobarbituric acid number, carbonyls, and diene values. Gas chromatograms (aromagrams) are also prepared The contract was extended in June 1964 to include analysis of headspace gas for carbon dioxide, carbon monoxide, oxygen, and pentane.

Analyses have been completed on samples drawn from storage after 34 months. Changes are occurring in nearly all factors being studied. The changes are influenced to a varying degree by all the variables of interest except type of wheat. Temperature exerts the most consistent influence However none of the tests specified in the original contract seem to correlate well with flavor score.

The headspace gas analyses, on the other hand, do show promise of being related to flavor score. This is particularly true for carbon-monoxide content of the headspace gas. Data for this

constituent are shown in Table 2.4 for all storage periods since this test was started. These data show a significant ($P < 1\%$) correlation with flavor score for all samples: the correlation coefficient is -0.6934. Because the carbon monoxide content of the headspace gas in nitrogen-packed samples is very low and in most cases zero (Figure 2.2), the correlation of flavor with CO in air-packed samples only may be more meaningful. When only the air-packed samples are included in the correlation, the coefficient is -0.5779. So, in either case, carbon-monoxide content of the headspace gas seems to predict flavor score reasonably well. This correlation may be expected to increase as greater differences in flavor scores develop.

Adjuncts

The contract to determine the stability of adjuncts in normal storage provides for taste-panel evaluation of twelve assorted supplements: apple topping, beef soup, butterscotch topping, chili sauce, chocolate pudding, cream of chicken soup, curry sauce, Oriental sauce, paprika gravy, raspberry jelly, strawberry spread, and wild cherry icing. Samples stored at 40°, 70°, and 100°F are compared with nitrogen-packed controls at -18°F. All adjuncts are packed in tin cans, with nitrogen atmosphere in half of the samples and air in the other half. Five adjuncts low in moisture are packed without desiccants; the other seven, higher in moisture, have half the samples packed with in-package desiccant (IPD) and half without. All adjuncts are being sampled at 6-month intervals over a period of 5 years.

Taste-panel evaluation

At the beginning of the storage study and at each test period all samples have been evaluated before, during, and after preparation, by an expert panel of four judges. Odor, texture, color, and ease of preparation are scored on a 6-point hedonic scale (0-normal to 5-extremely off).

After samples had been stored 30 months, the expert panel gave only slightly altered scores on preparation, in most cases. The differences were usually in the color of the dry mix or the rehydrated mix or both on samples stored at the higher temperatures. However, severe criticism (a score of 3 or higher) was given by the expert panel for certain attributes of some samples of apple topping, cream of chicken soup, Oriental sauce, and raspberry jelly. Air-packed apple topping stored at 100°F scored 3 on color of apple granules before, during, and after preparation; and the prepared mixture was too thin to keep apple granules suspended, as was the prepared N-packed apple topping which

TABLE 2.4.--Carbon monoxide content of headspace gas above bulgur wafers

(mean values for red and white wheat, peak area in mm^2)

Formulation[a]			Stored at 40°F months			Stored at 70°F months			Stored at 100°F months		
Cook	Binder	Pack	22	28	34	22	28	34	22	28	34
P	M	N	0	3	1	0	4	1	0	3	1
P	M	0	1	71	59	123	188	234	217	175	228
P	S	N	0	3	2	0	0	2	0	0	2
P	S	0	20	64	86	109	121	192	197	203	214
A	M	N	0	4	2	0	3	1	0	0	5
A	M	0	16	48	69	72	116	161	182	248	210
A	S	N	0	0	1	0	0	1	0	0	1
A	S	0	16	43	53	99	110	145	178	175	155

[a] Cook: P = pressure, A = atmospheric.

Binder: M = malt sirup, S = corn sirup.

Pack: N = nitrogen, 0 = air.

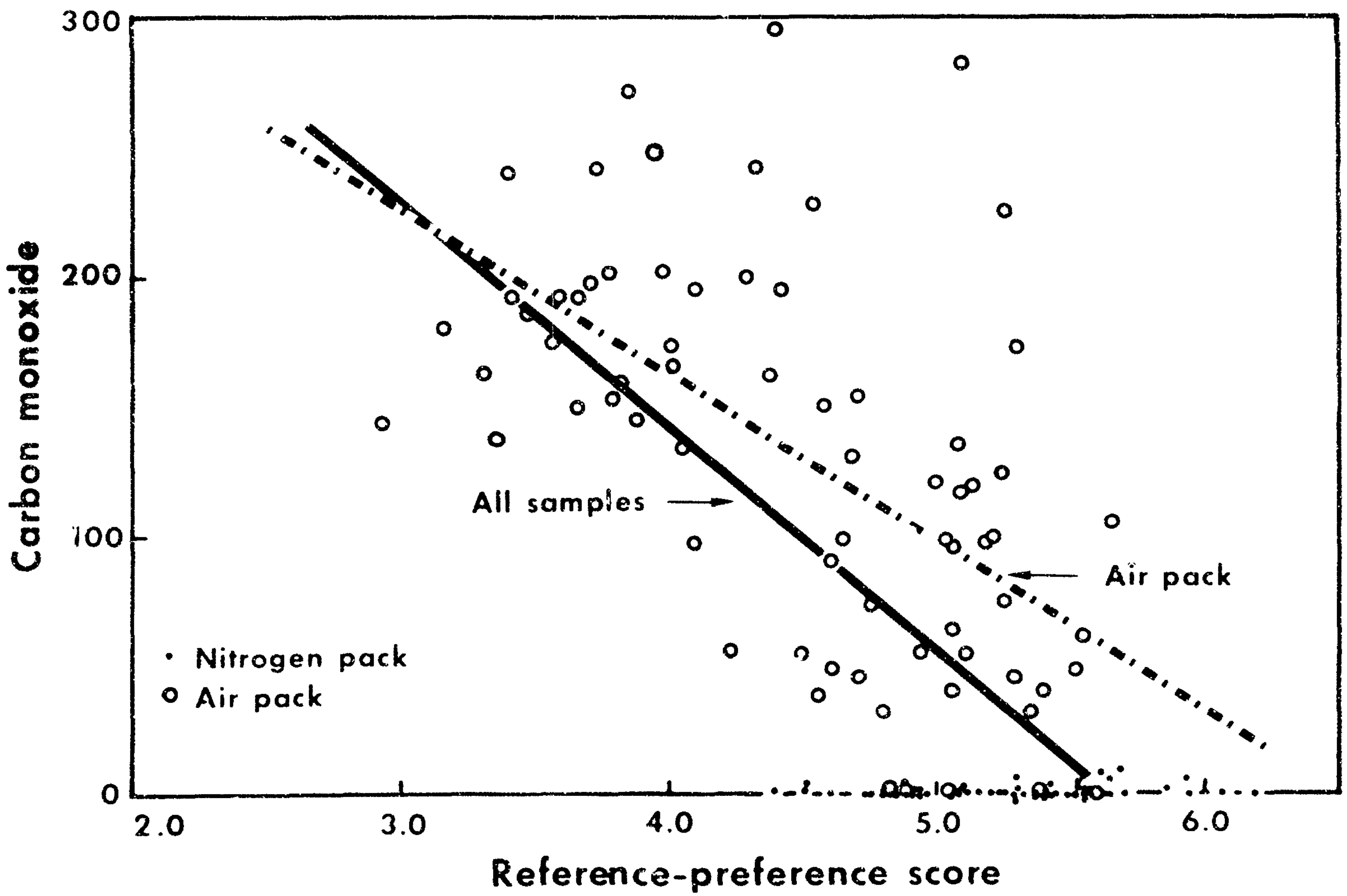

Figure 2.2 Relationship between carbon monoxide content of headspace gas and reference-preference score

had been held at 100°F. N-Packed and air-packed cream of chicken soup held at 100°F without desiccant scored 3 and 4, respectively, on color during and after preparation. Both samples also thickened after rehydration. All samples of Oriental sauce scored 3 for consistency after preparation period -- they were too thick for convenient serving. Both packs of raspberry jelly stored at 100°F scored 3 on color of dry mix and 4 on texture of dry mix -- they had caked in the cans.

Can corrosion was noted in some samples of curry sauce held at 70° and 100°F, in all samples of paprika gravy, and in all samples of Oriental sauce except the N-packs held at 40° and 70°F without desiccant.

Evaluations of flavor by a large panel using a 9-point hedonic scale have been completed on all samples after 30 months' storage. Mean flavor scores are given in Tables 2.5 and 2.6. The protective action of nitrogen packaging is shown by the flavor scores on all adjuncts except apple topping, wild cherry icing, strawberry spread, and beef soup. Among the seven adjuncts for which IPD is a treatment variable, samples with IPD scored higher for all except chili sauce, Oriental sauce, and beef soup. The effects of high temperature are especially demonstrated by the lower flavor scores given chicken soup, curry sauce, and Oriental sauce stored at 100°F.

In general, flavor scores are staying up reasonably well, at least for nitrogen-packed and/or IPD samples so that it would appear that ease of preparation (or actually lack of it) may be the first limiting factor for some of the adjuncts.

Chemical-physical determinations

On the samples possessing flow characteristics, Bostwick Consistometer readings are made in order to have objective measurement of changes in consistency during storage. Samples in which consistency was noted as altered by the panel of expert judges were also observed to be changing in Consistometer readings.

The headspace gas of all samples is being analyzed for carbon dioxide, and the headspace gas of nitrogen-packed samples for oxygen. When appreciable oxygen is detected in nitrogen packs, the samples are rejected and new ones drawn. Carbon dioxide first appeared in headspace gas of a few samples after they had been stored for 6 months at high temperatures. In fact, both samples of beef soup stored at 100°F without IPD were hard-swells with very high carbon dioxide content at 6 months; they had to be removed from the test. Carbon dioxide has continued to increase in all samples stored at 100°F with no desiccant, up to the 30-month check. Air-packed samples consistently developed more carbon dioxide than did nitrogen packs. No samples with IPD show any carbon dioxide, because the desiccant absorbs it.

TABLE 2.5.--Flavor scores for adjuncts packed without IPD, after 30 months' storage

Adjunct	Pack[a]	Storage temperature, °F -18	40	70	100	LSD[b]
Apple topping	A		5.85	6.30	5.80	NSD[c]
	N	6 00	6.18	5.92	5.78	
Butterscotch topping	A		6.28	6.40	5.62	0.46
	N	6.85	6.75	6.72	6.95	
Raspberry jelly	A		5.65	5.65	5.18	0.62
	N	5.45	5.78	6.20	6.35	
Strawberry spread	A		6.02	5.92	6.30	0.50
	N	5.52	6.02	5.28	5.65	
Wild cherry icing	A		6 20	6.22	5.98	NSD
	N	6.35	6.20	6.08	5.92	

[a] Packaging atmosphere: A = air, N = nitrogen.

[b] Least significant difference.

[c] No significant difference.

TABLE 26.--Flavor scores for adjuncts packed with and without IPD, after 30 months' storage

Adjunct	IPD[a]	Pack[b]	Storage temperature, °F -18	40	70	100	LSD[c]
Beef soup	0	A		6.50	6.28	[d]	
	0	N		6.25	6.26	[d]	0.62
	+	A		6.32	6.21	5.70	
	+	N	5.95	6.15	5.25	5.65	
Chili sauce	0	A		4.54	4.92	4.62	
	0	N		5.25	5.06	5.17	NSD[e]
	+	A		4.75	4.96	5.08	
	+	N	5.17	5.31	5.10	5.12	
Chocolate pudding	0	A		6.17	5.93	5.98	
	0	N		6.42	6.29	6.19	0.47
	+	A		6.33	6.64	6.58	
	+	N	6.62	6.96	6.73	6.90	
Cream of chicken soup	0	A		5.35	5.12	3.96	
	0	N		5.62	5.38	4.54	0.53
	+	A		6.06	6.42	5.38	
	+	N	6.35	5.90	6.38	6.27	
Curry sauce	0	A		4.44	4.54	4.15	
	0	N		5.21	4.75	4.50	0.58
	+	A		5.19	5.54	5.21	
	+	N	5.27	5.62	5.88	5.29	
Oriental sauce	0	A		5.08	5.40	4.21	
	0	N		5.65	6.02	4.35	0.57
	+	A		4.54	5.23	5.33	
	+	N	5.71	5.56	5.90	5.67	
Paprika gravy	0	A		3.92	3.94	3.65	
	0	N		5.46	5.15	4.00	0.60
	+	A		4.17	4.40	4.60	
	+	N	5.40	4.81	5.23	5.31	

[a] + = With in-package desiccant, 0 = without.

[b] Packaging atmosphere: A = air, N = nitrogen

[c] Least significant difference.

[d] Samples withdrawn from test.

[e] No significant difference

Beginning with the 24-month period, carbon monoxide content in the headspace gas has been measured Carbon monoxide, for the most part, parallels carbon dioxide in the samples without IPD but has the advantage that, because it is not absorbed by the IPD, it can be measured in all samples. Data for carbon monoxide content at 30 months are given in Tables 2.7 and 2.8.

Correlation coefficients between carbon monoxide contents of headspace gas and flavor scores of the twelve adjuncts have been calculated for the combined data from the samplings made at 24 and 30 months. Negative correlations were found for chocolate pudding, cream of chicken soup, curry sauce, and paprika gravy (significant at $P < 1\%$), and for apple topping, chili sauce, and Oriental sauce (significant at $P < 5\%$). Significant coefficients ranged from 0.4 to 0.6. Data from several more sampling periods are needed before a more positive statement can be made regarding the value of carbon monoxide as an indicator.

Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

TABLE 2.7.--Carbon monoxide content of headspace gas for adjuncts packed without MD, after 30 months' storage

Adjunct	Pack[a]	Storage temperature, °F			
		-18	40	70	100
Apple topping	A			12	116
	N	0	0	3	12
Butterscotch topping	A		1	9	28
	N	0	0	0	16
Raspberry jelly	A		0	3	33
	N	0	0	0	6
Strawberry spread	A		0	0	0
	N	0	0	0	0
Wild cherry icing	A		0	0	0
	N	0	0	0	0

[a] Packaging atmosphere: A = air, N = nitrogen.

TABLE 2.8.--Carbon monoxide content of headspace gas for adjuncts packed with and without IPD, after 30 months' storage

Adjunct	IPD[a]	Pack[b]	Storage temperature, °F -18	40	70	100
Beef soup	0	A		48	144	[c]
	0	N		6	6	[c]
	+	A		8	6	21
	+	N	0	0	0	0
Chili sauce	0	A		32	132	290
	0	N		6	0	3
	+	A		6	9	10
	+	N	0	0	0	0
Chocolate pudding	0	A		63	188	297
	0	N		6	9	9
	+	A		77	206	265
	+	N	0	5	6	6
Cream of chicken soup	0	A		6	21	318
	0	N		0	3	6
	+	A		6	6	c
	+	N	0	0	0	0
Curry sauce	0	A		18	64	168
	0	N		3	5	5
	+	A		3	0	0
	+	N	0	0	0	0
Oriental sauce	0	A		15	39	156
	0	N		0	8	3
	+	A		3	8	5
	+	N	0	0	0	0
Paprika gravy	0	A		[c]	[c]	225
	0	N		3	3	11
	+	A		16	20	[c]
	+	N	0	0	0	0

[a] + = With in-package desiccant, 0 = without.

[b] Packaging atmosphere: A = air, N = nitrogen.

[c] Data not obtained.

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13 ABSTRACT

Vapors from rancidifying bulgur and from autoxidized methyl linoleate, a model compound, are being further analyzed. Identification of oxidative products has been achieved principally by use of gas-liquid chromatography and mass spectrometry. Eleven acids have been identified from autoxidized methyl linoleate. Evidence has accumulated that early-appearing carbonyls are involved in secondary reactions that produce the more stable compounds appearing later in the oxidation process. The appearance of stable volatile components from oxidizing bulgur was coincident with oxygen uptake and off-flavor development. Pentane, carbon dioxide, carbon monoxide, and hexanal concentrations have generally followed a typical unsaturated fat oxidation curve. Oxygen uptake shows a similar curve. Hexanal levels in puffed bulgur stored under oxygen at elevated temperatures did not parallel off-flavor development over long storage periods.

Long term (five-year) storage studies of bulgur wafers and adjuncts are continuing. Taste panel evaluations for the wafer through 40 months continue to show a protective influence of nitrogen packing on flavor of wafers stored at 70° and 100° F. Other treatment variables are relatively unimportant. Not even for wafers stored at 70° and 100° F. have the scores dropped to a hedonic score as low as 4 (dislike slightly). Of the objective tests being investigated for surveillance testing, carbon monoxide content of the headspace gas seems to be the most promising. In general, flavor scores for adjuncts are remaining reasonably high, at least for nitrogen-packed and for IPD samples. It may be that ease of preparation (or actually lack of it) may be the first limiting factor for some adjuncts. Carbon monoxide content of the headspace gas above the adjuncts has been found to correlate with flavor score for seven of the adjuncts.

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Wheat						
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Storage Stability						
Fallout Shelters						
Sauces and Spreads						
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